

Effect of sodium dodecyl sulfate on the reactivity of copper(II) complexes with 2-dimethylaminomethylphenol

I. S. Ryzhkina,^{a*} L. A. Kudryavtseva,^a G. A. Boos,^b and Yu. I. Sal'nikov^b

^aA. E. Arbusov Institute of Organic and Physical Chemistry, Kazan' Scientific Center of the Russian Academy of Sciences,

8 ul. Akad. Arbuzova, 420083 Kazan', Russian Federation.

Fax: +7 (843 2) 752 253

^bKazan' State University, 18 ul. Lenina, 420008 Kazan', Russian Federation.

Fax: +7 (843 2) 380 122

The effects of the anionic surfactant sodium dodecyl sulfate on complex formation of 2-dimethylaminomethylphenol (**1**) with copper(II) in aqueous solutions and on the kinetics of the reactions of copper(II) complexes of **1** with 4-nitrophenylbis(chloromethyl)phosphinate (**2**) were studied. The reactivities of the complexes in these reactions are higher than that of **1** at all concentrations of SDS studied (0.010–0.200 mol L⁻¹) with pH 7–9.

Key words: complex formation, kinetics; sodium dodecyl sulfate, copper(II), 2-dimethylaminomethylphenol.

It is known¹ that the bifunctional nucleophile 2-dimethylaminomethylphenol (**1**) and its copper complex are catalysts of hydrolysis of esters of phosphorus acids. We have shown² that sodium dodecyl sulfate (SDS) inhibits the reaction of **1** with 4-nitrophenylbis(chloromethyl) phosphinate (**2**) mainly due to suppression of the formation of reactive zwitterionic (HL[±]) and phenolate (L⁻) forms of compound **1** as a result of the shift of acid-base and tautomeric equilibria. The nonreactive form of **1** protonated at the nitrogen atom (H₂L⁺) is mainly present in solution in the pH 7–9 range studied. In the absence of a surfactant, the reactivity of the copper complex of compound **1**, which is reactive in the neutral pH range, is considerably higher than that of ligand **1**, and the mechanisms of their effects differ.¹ The effects of SDS in forming anionic micelles upon complex formation of **1** with copper(II) and on the reactivity of the complexes formed in the reaction with substrate **2** are studied in this work.

Experimental

Compound **1** (HL) was synthesized by the known procedure.³ SDS was purified and **2** was prepared according to the previously published procedures (see Refs. 4 and 5, respectively). Copper(II) nitrate (reagent grade) was used. The ionic medium was formed by the components of the solution. Complex formation in the copper(II)–ligand **1** system in the presence of SDS was studied at 20±0.1 °C both spectrophotometrically and pH-metrically. The equilibria were simulated by the CPESSP program.⁶ The simulation is based on the determination of the minimum value of the sum of deviation squares (the

nonlinear least-squares method) calculated from the experimentally determined characteristics for all points upon movement along the coordinate, which determines the composition of the equilibrium system (pH, concentration of the ligand, etc.). The optical density of solutions was measured on a Specord UV-VIS spectrophotometer (the length of the absorbing layer was 1 cm), and the pH values of the solutions were measured on a pH-340 instrument. The complexes of copper(II) with **1** are insoluble in an aqueous solution but soluble in the presence of SDS. The dissolution of the complexes results in the appearance of a band with a maximum at 426 nm in the absorption spectrum. The reaction kinetics was studied under pseudo-first-order conditions by increase in the optical density due to the formation of *p*-nitrophenolate (λ 400 nm) at 25±0.1 °C. The observed rate constants (*k*_{obs}) were calculated by a first-order equation by the least-squares method using the known program^{1,7} (the correlation coefficient was not lower than 0.99). The errors of determination of the apparent equilibrium and stability constants of the complexes were not higher than 0.2 logarithmic units.

Results and Discussion

Investigation of the kinetics of reactions involving metal complexes is closely related to the determination of their structure and the most important quantitative parameters of their complex formation in solutions. This problem becomes more urgent when surfactants are introduced into solution, because it is known^{8,9} that they substantially affect reactions of metal ions with organic reagents. Therefore, the complex formation of compound **1** with copper(II) should be studied for the investigation of the kinetics of the reaction of substrate **2** with copper complexes **1**.

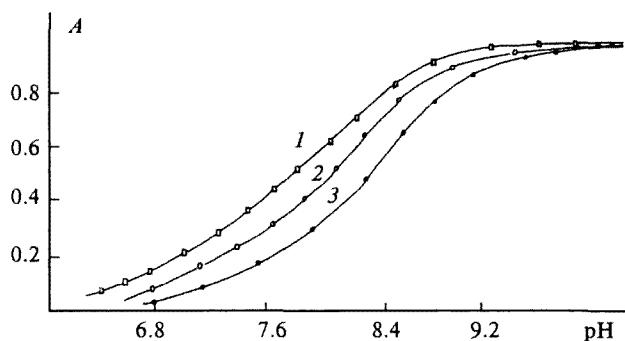
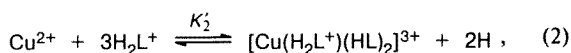
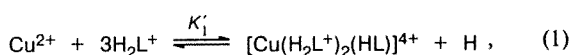


Fig. 1. Dependence of the optical density of the solution at λ_{\max} 426 nm ($C_{\text{Cu}^{2+}} = 5.8 \cdot 10^{-4}$, $C_1 = 1 \cdot 10^{-2}$ mol L $^{-1}$) on pH of the medium at various concentrations of SDS/mol L $^{-1}$: 0.01 (1); 0.025 (2); 0.1 (3).

The pH values were varied from 6.0 to 10.2 in five series of solutions with fixed concentrations of copper(II) ($5.8 \cdot 10^{-4}$ mol L $^{-1}$) and **1** (0.01 mol L $^{-1}$). The constant concentration of SDS was maintained in each series of the solutions. The A -pH dependences are presented in Fig. 1.

The value of the optical density (A) dependent of pH or the concentration of the ligand at the fixed pH value was used as the modelled response. In the case of the inverse problem with various stoichiometric matrices solved according to the CPESP program, the adequate description of the experimental data (the estimation was performed by the Fischer criterion¹⁰) is achieved when equilibrium processes (1) and (2) are the determining reactions of complex formation:



where H_2L^+ and HL are the protonated at the nitrogen atom ($\text{p}K_1$) and neutral ($\text{p}K_2$) forms of compound **1**, respectively.

Table 1. Values of apparent equilibrium constants of reactions (1) and (2) and of stability constants of the complexes

C_{SDS} /mol L $^{-1}$	$-\log K'_1$	$-\log K'_2$	$\log \beta_1$	$\log \beta'_1$	$\log \beta_2$	$\log \beta'_2$
0.004	0.29	8.41	8.46	6.06	9.09	6.69
0.01	1.11	9.34	7.84	5.84	8.56	6.56
0.025	0.79	8.95	8.96	7.36	10.55	8.95
0.10	1.18	9.83	8.82	7.72	10.17	9.17
0.16	0.08	8.46	9.92	9.12	11.54	10.74

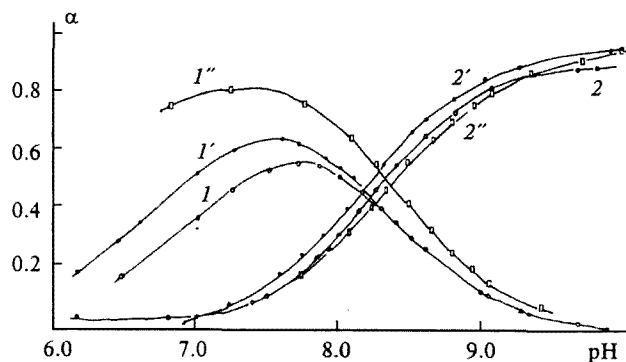


Fig. 2. Dependence of the relative content of complex forms **3** (1) and **4** (2) on pH of the medium ($C_{\text{Cu}^{2+}} = 5.8 \cdot 10^{-4}$ mol L $^{-1}$, $C_1 = 1 \cdot 10^{-2}$ mol L $^{-1}$) at various concentrations of SDS/mol L $^{-1}$: 0.01 (1, 2); 0.025 (1', 2'); 0.16 (1'', 2'').

Thus, two types of complex species are formed in the solutions studied: depending on pH of the medium, the species contain in the coordination sphere either two protonated ligands H_2L^+ and one neutral ligand (complex **3**) or one protonated and two neutral ligands (complex **4**).

The values of apparent dissociation constants of compound **1**, $\text{p}K_1$ and $\text{p}K_2$, determined at the corresponding SDS concentrations¹¹ were used for the calculation of the apparent equilibrium constants K'_1 and K'_2 (Table 1).

The equilibrium constants of reactions (1) and (2) should be considered as estimation values, because the ionic strength of the solutions was not maintained constant. The values of apparent stability constants of the complexes (β) calculated from Eqs. (3) and (4) are also presented in Table 1.

$$\log \beta_1 = \log K'_1 + \text{p}K_1, \quad (3)$$

$$\log \beta_2 = \log K'_2 + 2\text{p}K_1. \quad (4)$$

The dependence of the relative content of each form (in fractions of the total concentration of copper(II)) on pH of the medium is presented in Fig. 2.

The effect of the concentration of compound **1** ($C_{\text{HL}} = 2.0 \cdot 10^{-3}$ – $2.6 \cdot 10^{-2}$ mol L $^{-1}$) on the complex formation at the fixed pH value equal to 8.6 is also considered (Fig. 3). Under these conditions, the $[\text{Cu}(\text{H}_2\text{L}^+)(\text{HL})_2]^{3+}$ complex predominates in the solution. The values of the logarithm of the equilibrium constant K'_2 calculated on the basis of the experimental dependences A -pH and A - C_{HL} (pH 8.60) were -9.29 ($C_{\text{SDS}} = 0.01$ mol L $^{-1}$) and -10.05 ($C_{\text{SDS}} = 0.10$ mol L $^{-1}$) and almost coincided with the data presented in Table 1.

It is known¹² that $\text{Cu}(\text{DS})_2$ predominates on the micellar surface in the system containing SDS and copper(II), because the bicharged copper ion is stronger

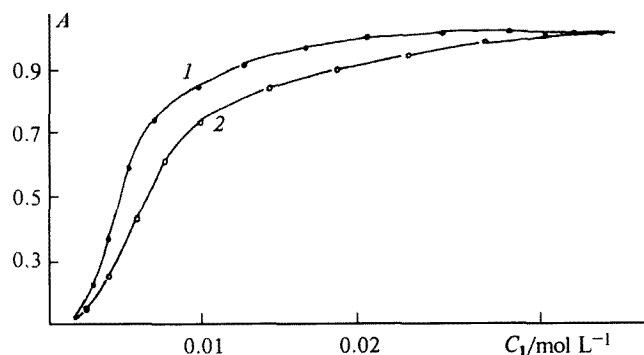
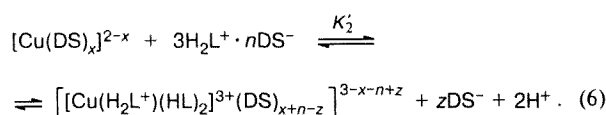
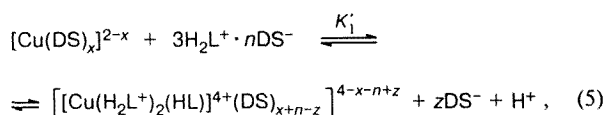


Fig. 3. Dependence of the optical density of the solution at λ_{\max} 426 nm on C_1 (pH 8.6) at various concentrations of SDS/mol L⁻¹: 0.01 (1); 0.10 (2).

attracted by the adsorption monolayer of dodecyl sulfate ions than the sodium ion. However, we failed to determine quantitative parameters of the reaction of copper(II) with the dodecyl sulfate anion (DS⁻) under the experimental conditions ($C_{\text{Cu}^{2+}} = 5.8 \cdot 10^{-4}$ mol L⁻¹) due to low changes in the optical density of the solutions at $C_{\text{SDS}} = 0 \div 0.025$ mol L⁻¹. A precipitate was formed at the higher concentrations of SDS.

It is seen from the data in Table 1 that the equilibrium constants K_1' and K_2' depend on the concentration of the DS⁻ ion in the whole range of the surfactant concentrations studied. This circumstance is reflected by the refined schemes of the reactions of complex formation (Eqs. (5) and (6)):



The stability constants of both complexes were calculated taking into account the concentration of the DS⁻ ion (Eqs. (7) and (8)):

$$\log \beta_1' = \log K_1' + pK_1 + \log[\text{DS}^-], \quad z = 1 \quad (7)$$

$$\log \beta_2' = \log K_2' + 2pK_1 + \log[\text{DS}^-], \quad z = 1. \quad (8)$$

It turned out that the equilibrium constants of both complexes (β_1' and β_2') are unchanged in the range of SDS concentrations from 0.004 to 0.01 mol L⁻¹. At these

SDS concentrations, its critical micelle formation concentration (CMC) is not reached yet. At $C_1 = 5 \cdot 10^{-3}$ mol L⁻¹, CMC of SDS is ~ 0.02 mol L⁻¹ (see Ref. 2). In the range of SDS concentrations from 0.025 to 0.1 mol L⁻¹, which are higher than CMC, the values of $\log \beta_1'$ and β_2' are also constant within the determination error, but are considerably higher. The reason for this may be the change in the "environment" of the complex, *i.e.*, in the medium that surrounds the complex. When the SDS concentration is lower than 0.01 mol L⁻¹, the complex formation occurs in the aqueous solution containing ions of the surfactant, while when CMC is reached, the complexes exist in the medium with the lower polarity than that of water. The properties of the area of localization of reagents in micelles resemble those of a mixture of water with an aprotic solvent.¹³ A sharp increase in the stability of the complexes at the SDS concentration of 0.16 mol L⁻¹ is probably caused by structural changes in the micelle itself.¹²

Thus, the process of complex formation in the micellar system exhibits some specific features. Unlike solutions in aqueous ethanol¹⁴ in which only one complex species $[\text{CuHL}]^{2+}$ is formed, the introduction both of cationic and nonionic surfactants¹⁵ makes the composition of the complex more complicated. An increase in the number of coordinated ligands in the presence of the surfactant is explained by loosening the hydrate shell of the metal ion due to hydrophobic hydration and is known in the literature.⁷

DS⁻ anions of the external sphere of the complex compound favor the coordination of protonated ligands. It also cannot be excluded that the protonated complex in the micellar pseudo-phase is stabilized by the formation of hydrogen bonds with oxygen atoms of the surfactant. In addition, the relatively high stability of protonated complexes could be the result of interplanar interaction (stacking¹⁵) of benzene rings of coordinated aminomethylphenols. A decrease in the surface tension of water due to the surfactant decreases the power consumed for creation of the cavity in the solution.

Axial positions of the complex forming agent are blocked due to the stacking. In the equatorial plane, copper(II) coordinates a water molecule of those entering the composition of the micelle along with three ligands mentioned.

The observed first-order rate constants of the reaction of 1 with 2 in the absence and in the presence of copper(II) were determined at varied SDS concentrations and the fixed value of pH 8.0 (Fig. 4). The effect of pH of the solutions at constant concentrations of the surfactant on the values of rate constants is also considered (Fig. 5). It is established that SDS inhibits these reactions. The dependences $k_{\text{obs}} = f(C_{\text{SDS}})$ reach a plateau as the content of SDS increases (see Fig. 4); however, the observed rate constants of the reactions of 1 with 2 in the presence of copper(II) are higher than those without copper(II) in the whole range of SDS concentrations

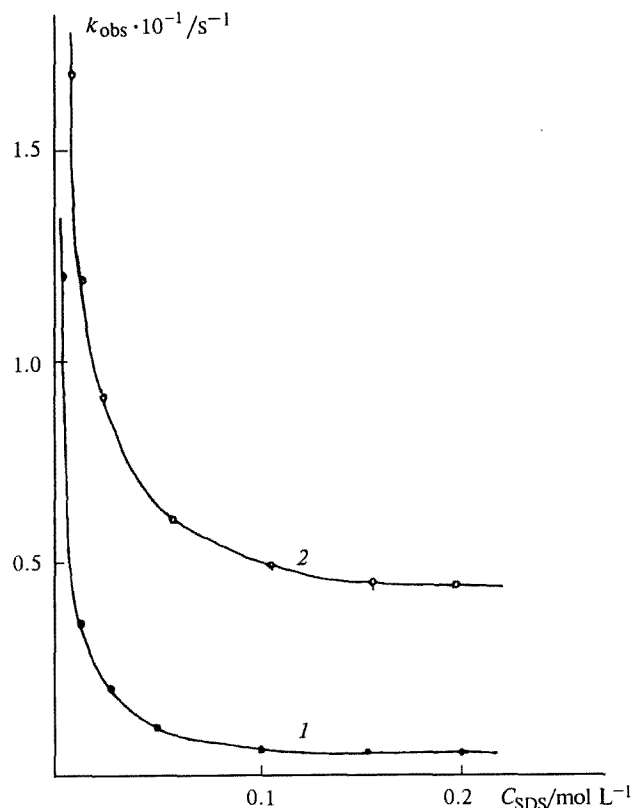


Fig. 4. Dependence of the observed rate constants of the reaction of **1** with **2** ($C_1 = 1 \cdot 10^{-2} \text{ mol L}^{-1}$, pH 8.0) on the concentration of SDS in the absence (**1**) and in the presence (**2**) of copper(II) ($C_{\text{Cu}^{2+}} = 5.8 \cdot 10^{-4} \text{ mol L}^{-1}$).

studied at $\text{pH} \geq 6$ (see Figs. 4 and 5). An increase in k_{obs} is associated first of all with the formation of reactive complexes **3** and **4**, while the phenomenon of the "salt effect" that takes place in micellar solutions of SDS¹⁶ is observed at considerably higher concentrations of cations (0.1–1 mol L⁻¹) than in our case.

The concentrations of complexes **3** and **4** ($C_K = \alpha \cdot C_{\text{Cu}^{2+}}$) in the pH range corresponding to the

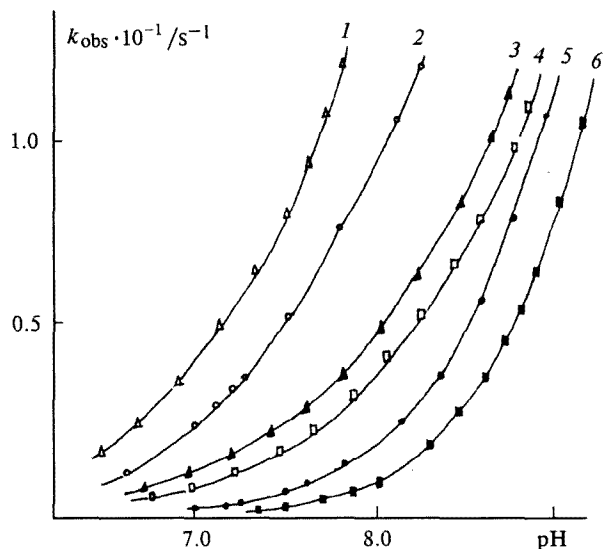


Fig. 5. Dependence of the observed rate constants of the reaction of **1** with **2** ($C_1 = 1 \cdot 10^{-2} \text{ mol L}^{-1}$) on pH of the medium in the absence (**2**, **4**, **6**) and in the presence of copper(II) ($C_{\text{Cu}^{2+}} = 1.9 \cdot 10^{-4} \text{ mol L}^{-1}$) (**1**, **3**, **5**) at various concentrations of SDS/mol L⁻¹: 0.01 (**1**, **2**); 0.025 (**3**, **4**); 0.2 (**5**, **6**).

maximum accumulation of the complexes were calculated on the basis of the fractional distribution of these complexes (see Fig. 2). The effective second-order rate constants of the reactions of complexes **3** (k_2^3) and **4** (k_2^4) were determined from the dependence $k_{\text{obs}} = f(\text{pH})$ (see Fig. 5) at the SDS concentrations of 0.01, 0.025, and 0.02 mol L⁻¹ by the formula $k_2 = (k_{\text{obs}} - k_{\text{obs}}^1) / C_K$, where k_{obs}^1 are the observed rate constants of the reaction of **1** with **2** without copper(II) under identical conditions (Table 2). It follows from the data in Table 2 that the reactivity of both complexes decreases as the SDS concentration increases from 0.01 mol L⁻¹, at which CMC is not reached yet, to 0.20 mol L⁻¹, at which the observed rate constants are approximately equal to those

Table 2. Effective rate constants of the reactions of complexes **3** and **4** with **2** in the presence of SDS*

pH	α	$C_3 \cdot 10^{-4}$ /mol L ⁻¹	k_2^3 /mol ⁻¹ L s ⁻¹	pH	α	$C_4 \cdot 10^{-4}$ /mol L ⁻¹	k_2^4 /mol ⁻¹ L s ⁻¹
$C_{\text{SDS}} = 0.025 \text{ mol L}^{-1}$							
7.0	0.52	1.0	238	8.6	0.73	1.4	786
7.1	0.56	1.1	259	8.8	0.80	1.5	784
			248*				785*
$C_{\text{SDS}} = 0.200 \text{ mol L}^{-1}$							
6.8	0.75	1.4	46	8.6	0.62	1.2	416
7.0	0.80	1.5	51	8.8	0.72	1.4	428
			48*				422*

Note. At $C_{\text{SDS}} = 0.010 \text{ mol L}^{-1}$ $k_2^3_{\text{av}} = 418 \text{ mol}^{-1} \text{ L s}^{-1}$, calculated at pH 6.8, 7.0.

* Average values.

in the micellar pseudo-phase. This is probably associated with several factors, one of which is a decrease in the polarity of the medium in the micellar pseudo-phase compared to that of water, which also affects the values of the stability constants of the complexes. The similar tendency of the effect of the nature of the medium on the stability constants and the reactivity of the complexes has been observed previously.⁷

In addition, high positive charges of complexes **3** and **4**, which should facilitate the polarization of the substrate upon solubilization by negative SDS micelles, are probably neutralized.

The comparison of constants k_2^3 and k_2^4 testifies that the reactivity of complex **4** is 3 to 10-fold higher than that of complex **3**. Even when the SDS concentration increases approximately by an order of magnitude, its inhibiting effect considerably less affects the reactivity of complex **4** (k_2^4 decreases ~1.5-fold) than that of complex **3** (k_2^3 decreases ~6-fold). The higher reactivity of complex **4** can be caused by the fact that its first coordination sphere contains two hydroxyl groups of neutral forms of the ligands activated by the coordination with copper(II) that play a role of a nucleophile, while the first coordination sphere of complex **3** contains one this group.

It is noteworthy that the coordination of substrate **2** by the complexes is difficult compared to the aqueous-ethanol solution¹⁴ due to the complication of the composition of the aminomethylphenol complexes. Nevertheless, the presence of the mobile water molecule in the coordination sphere of the complexes creates prerequisites for their contact with a substrate.

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